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# Recent advances in the biogeochemistry of nitrogen in the ocean

**S. W. A. Naqvi<sup>1</sup>, M. Voss<sup>2</sup>, and J. P. Montoya<sup>3</sup>**

<sup>1</sup>National Institute of Oceanography, Dona Paula, Goa 403 004, India

<sup>2</sup>Baltic Sea Research Institute, Seestrasse 15, 18119 Rostock, Germany

<sup>3</sup>School of Biology, Georgia Institute of Technology, Atlanta GA 30332, USA

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Correspondence to: S. W. A. Naqvi (naqvi@nio.org)

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Until fairly recently, study of the marine nitrogen cycle was considered to be important but a bit dull. Important because nitrogen had long been recognized as an essential nutrient that often limits primary production in the ocean but dull because the residence time of fixed nitrogen in the ocean was believed to be long (~10 000 yr; Emery et al., 1955), and its budget, like those of most other elements, at or very near steady state. Serious efforts to quantify the key terms in the combined nitrogen budget – denitrification and nitrogen fixation – began in the 1970s, and despite varying estimates provided by different investigators, the notion of a steady state began to be challenged in the mid-1980s (Codispoti and Christensen, 1985, and references therein). The discovery of large glacial-interglacial changes in atmospheric carbon dioxide content based on analyses of polar ice cores (Delmas et al., 1980), arguably one of the most important findings in Earth Sciences in recent years, left paleoclimatologists scrambling for an explanation, and one of the earliest hypotheses offered invoked changes in the fixed nitrogen inventory of the oceans (McElroy, 1983), subsequently refined by Altabet et al. (1995) and Ganeshram et al. (1995). However, the extent to which variations in denitrification or nitrogen fixation can drive changes in nitrogen inventory (Falkowski, 1997) that contribute to climatic cycles, and whether or not the nitrogen budget in today's ocean is balanced, are issues that remain unsettled (Sigman and Boyle, 2000; Codispoti et al., 2001; Gruber, 2004).

The interest in the balance (or lack thereof) between the input and loss terms of the oceanic nitrogen budget has led to a broad range of studies including focused biological measurements of specific processes (e.g.,  $N_2$ -fixation and denitrification), basin-scale geochemical measurements, and integrative modeling (Gruber and Sarmiento, 1997; Brandes et al., 1998; Brandes and Devol, 2002; Deutsch et al., 2004, 2007; Sigman et al., 2005; Devol et al., 2006), and consequently marked improvements in flux estimates. Recent research on the nitrogen cycle has also uncovered new players and processes on both the supply and demand sides of the nitrogen cycle (Brandes et al., 2007). The rapidly increasing application of molecular tools during the last two decades has provided new insights into the composition and structure of various mi-

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5 microbial communities involved in the nitrogen cycle (Zehr and Ward, 2002; Ward, 2005). For example, on the supply side, DNA sequence analysis has revealed a diverse community of N<sub>2</sub> fixing organisms in coastal and oceanic waters (Zehr et al., 1998, 2001; Falcon et al., 2004), many of which have not been isolated. Some of these recently

10 discovered N<sub>2</sub> fixers show very high rates of N<sub>2</sub> fixation in the water column and we are only now developing an appreciation for their importance in supplying combined nitrogen to the ocean through studies that integrate molecular and biogeochemical techniques (Montoya et al., 2004; Zehr et al., 2007).

Perhaps the most important recent finding on the demand side is the discovery of

15 anaerobic ammonium oxidation (anammox), a dissimilatory process involving reaction of ammonia with nitrite (Strous et al., 1999). Anammox provides an additional pathway of conversion of fixed nitrogen to the relatively inert elemental form (N<sub>2</sub>). Evidence for the importance of this process is rapidly accumulating from both enclosed basins (Dalsgaard et al., 2003; Kuypers et al., 2003) and oxygen minimum zones (OMZs)

20 of the open ocean (Kuyper et al., 2005; Thamdrup et al., 2006; Nicholls et al., 2007; Hamersley et al., 2007). In fact, in almost all of the open ocean studies, anammox has been found to be the dominant process with very little contribution coming from heterotrophic denitrification. This is surprising because the nitrite used for anammox should be largely derived from nitrate reduction (i.e., heterotrophic denitrification), although a coupling between nitrification and anammox has also been reported from the

25 upper portion of the Black Sea suboxic zone (Lam et al., 2007). Whether or not the apparent lack of further reduction of nitrite to N<sub>2</sub> by heterotrophic denitrifiers is real and as widespread as these recent reports suggest, or it is a methodological artifact, still remains to be established. If heterotrophic denitrification is truly as unimportant as these studies suggest, the mechanisms and pathways of organic matter degradation in oceanic suboxic zones becomes a very important question. In contrast, both anammox and heterotrophic denitrification have been found to be important in sediments (Trimmer et al., 2006). Interestingly, intracellular accumulation of nitrate and complete denitrification to N<sub>2</sub> has been reported for the benthic foraminifer *Globobulimina pseu-*

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*dospinescens* (Risgaard-Petersen et al., 2006), one of the few eukaryotes known to be capable of denitrification.

Additional modes of loss of fixed nitrogen could also occur through reactions of nitrate (or nitrite) with other reduced chemical species, although their quantitative importance is probably much smaller. Reactions involving reduced metal species (primarily  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$ ) are thermodynamically feasible and can be coupled to metal reduction reactions to drive denitrification with no net consumption of metal ions (Luther et al., 1997), but convincing evidence for their occurrence in the environment is lacking so far. On the other hand, several studies have shown that a number of sulphur bacteria (e.g. *Thioploca*, *Beggiatoa* and *Thiomargarita*) accumulate high concentrations of nitrate within their vacuoles when at the sediment-water interface, then migrate downward through the sedimentary redox gradient to access sulphide, which they oxidize with their intracellular store of nitrate (Fossing et al., 1995; Schulz et al., 1999). This behaviour results in injection of oxidant much deeper into the sediment column than could be reached by diffusive fluxes alone.

Finally, interest in the nitrogen cycle has also been rekindled by the large extent to which it has been impacted by human activities. Production of synthetic fertilizers, fossil fuel combustion, and cultivation of leguminous crops have approximately doubled the input of combined nitrogen to the terrestrial nitrogen cycle, and the supply of fixed nitrogen to the sea in all probability has also undergone a similar enhancement since the Industrial Revolution (Galloway et al., 2004). This has led to the appearance of oxygen deficiency in several coastal areas and intensification of some naturally hypoxic systems, impacting nitrogen redox processes including the production of nitrous oxide (Naqvi et al., 2000). The business-as-usual projections for future for terrestrial nitrogen loading to coastal ecosystems paint a bleak picture (Seitzinger et al., 2002).

It is apparent from the above overview that the marine nitrogen cycle is more dynamic (with the turnover time of fixed nitrogen now believed to be ~1500 yr; Codispoti et al., 2001), less well understood, and much more exciting than previously thought. However, despite impressive and rapid advances in our understanding of many impor-

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tant aspects of the marine nitrogen cycle, there are a number of fundamental issues that remain unresolved. Therefore, a broad synthesis of the current state of our knowledge is both timely and necessary as it would serve as a tool for channeling future research efforts in the right direction. Keeping this in view, we organized an international workshop, “Significant Processes, Observations, and Transformation in Oceanic Nitrogen (SPOT-ON)” at the Institute for Baltic Sea Research, Warnemünde, Germany, from 26 June to 1 July 2005. Sponsored by the Deutsche Forschungsgemeinschaft (DFG), the overarching goal of SPOT-ON was to delineate the major current uncertainties and gaps in our fundamental understanding of the oceanic nitrogen cycle. The workshop was organized around a series of major themes, with invited and contributed papers in each area. Some of the papers presented at the Workshop have already been published elsewhere (e.g., Devol et al., 2006; Johnson et al., 2006; Moisander et al., 2006; Thamdrup et al., 2006; Westley et al., 2006; Brunelle et al., 2007; Casciotti and McIlvin, 2007; Deutsch et al., 2007; Hamersley et al., 2007; Paerl et al., 2007; Yamagishi et al., 2007). The remaining papers, which deal with diverse aspects of the nitrogen cycle are included in this issue. Here we provide a brief overview of some of the major highlights of SPOT-ON, with particular reference to papers published in this volume.

## 1 Theme: the global N cycle

The oceanic fixed nitrogen balance (or the lack thereof), continues to be a topic of intense debate. As in Codispoti et al. (2001), Codispoti (2007) argues for a high rate of fixed nitrogen loss ( $\sim 400 \text{ Tg N yr}^{-1}$ ) from today's oceans, a view again contested by Gruber (2006) and Sarmiento (2006) in their reviews of this manuscript. Among other things, Codispoti bases his high estimates on measurements of  $\text{N}_2/\text{Ar}$  ratios in oxygen minimum zones, which should reflect the total production of  $\text{N}_2$  via denitrification, but Gruber questioned the general applicability of these results. Sarmiento, on the other hand, considered the sedimentary denitrification rate estimate arrived at by Codispoti

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to be too high.

One major point of contention is the relative importance of sedimentary and water column denitrification. Brandes and Devol (2002) proposed an isotopic approach to partition denitrification between the sediments and the water column based on the observation that denitrification in the water column involves much greater expression of isotopic fractionation than sedimentary denitrification. Using the observed mean nitrogen isotopic composition of nitrate in the ocean ( $\sim 5\%$ ) Brandes and Devol showed that the ratio between sedimentary and water column denitrification should be  $\sim 3.5:1$ . However, Deutsch et al. (2004) pointed out that since the oceanic waters are not well mixed and denitrification and  $N_2$ -fixation are dominant in well-defined and often different geographical areas, the dilution effect will lower this ratio to  $<3$ . Altabet (2007) further argues that due to other factors (conversion of organic N to  $N_2$ , Rayleigh closed and open system effects) the effective discrimination factor for denitrification in the water column is only about half of its inherent microbial value, and so the sedimentary to water column ratio should be accordingly lower. The application of this ratio in constraining the total oceanic denitrification thus seems to have severe limitations. There is also a possibility, as Codispoti points out, that the water column denitrification rates in today's ocean, based as they are on observations made only over the past few decades, could also have been enhanced by human activities. Should this be the case then the isotopic signal would not have propagated throughout the ocean, and hence one cannot constrain the total oceanic denitrification rate from the current isotopic composition of nitrate in the ocean.

There were several papers dealing with modeling presented at the SPOT-ON Workshop including the one by Deutsch et al. (2007) that made use of the distribution of  $P^*$  (a tracer similar to the  $N^*$  introduced by Gruber and Sarmiento, 1997) to estimate  $N_2$ -fixation rates in the ocean. A major conclusion of this study is that the zones of  $N_2$ -fixation and denitrification are not geographically separated, as has been believed so far (Gruber and Sarmiento, 1997). This is because denitrification creates an excess of phosphate that should stimulate  $N_2$  fixation. This linkage is not always apparent,

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however, as shown by the North Atlantic, which accounts for only a small fraction of the global water-column denitrification but has long been recognized as a major region of  $N_2$ -fixation. Mills et al. (2004) found co-limitation of  $N_2$ -fixation in this region by P and iron. As another modeling component of SPOT-ON, that is included in this issue, Coles and Hood (2007) utilize a coupled physical-biogeochemical model that explicitly includes P and iron dynamics (in addition to nitrogen cycling) to simulate  $N^*$  distribution in the North Atlantic. The model can reproduce the large scale  $N^*$  anomaly patterns but requires a high  $N_2$  fixation rate ( $3.4 \times 10^{12}$  moles  $N yr^{-1}$  between Lats.  $25^\circ S$  to  $65^\circ N$ ). Coles and Hood argue for an upward revision of  $N_2$  fixation rate estimate for the ocean in order to help resolve the apparent imbalances in the global nitrogen budget.

## 2 Theme: supply of N to the ocean

Jickells (2006) provides a comprehensive review of the available information on atmospheric deposition of various forms of nitrogen over the ocean, and the effects of this deposition on the marine environment both in coastal and offshore areas. Jickells demonstrates that, due to the anthropogenic enhancement, atmospheric inputs to the ocean are now comparable with riverine fluxes of dissolved inorganic nitrogen. This paper also examines the management strategies required to reduce atmospheric nitrogen loading, emphasizing different strategies for ammonia/ammonium and nitric acid/nitrate, with the former requiring local regulation but the latter necessitating a regional approach.

$N_2$  fixation is clearly an important source of combined N to the ocean, and a number of papers focus on this process. Ohlendieck et al. (2007) present results of new measurements of  $N_2$ -fixation rates with concomitant estimates of primary production for two summers in the Baltic Sea that indicate a somewhat larger contribution of  $N_2$ -fixation to new production than previously believed. Large geographical and interannual variability observed in this study appears to be driven by temperature and vertical stratification. Analyses of  $N_2$  fixation rates by various size classes of diazotrophs reveal that organ-

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isms  $>5\mu\text{m}$  in size account for most of the  $\text{N}_2$  fixation. These C:N uptake ratios by the diazotrophs are higher than the Redfield values, but ratios in filamentous bacterial cells were a little lower indicating either carbon release by the diazotrophs or additional uptake of regenerated nitrogen.

5 Most of the research on  $\text{N}_2$ -fixation in the ocean has focused on the larger organisms, especially the filamentous, colonial *Trichodesmium* that forms extensive and striking blooms in the tropics and subtropics. However, recent work has highlighted the potential importance of unicellular diazotrophs (Zehr et al., 2001; Montoya et al., 2004). Montoya et al. (2007) investigate relative contributions of *Trichodesmium* and such smaller  
10 organisms to diazotrophy in the tropical Atlantic Ocean using previously published and new data. Their results reveal significant and systematic differences between the eastern and western regions with *Trichodesmium* dominating diazotrophy in the west and the other unidentified small organisms becoming more important in the east, with the overall nitrogen fixation rate being more or less invariable zonally. However, the cause  
15 of the observed trend remains to be investigated.

A number of articles in this issue concentrate on specific issues related to  $\text{N}_2$  fixation. Based on laboratory cultures of *Trichodesmium* grown at different temperatures, Breitbarth et al. (2007) show that the typical correlation of *Trichodesmium* abundance with ambient water temperature arises primarily from the direct physiological effects  
20 of temperature on the growth of this genus. Combining their results with the model-derived change in sea surface temperatures (SSTs) for the future, the authors predict a reduction of  $\text{N}_2$  fixation by *Trichodesmium* due to global warming. However, it is unclear how the overall rate of  $\text{N}_2$  fixation will be affected by climate change because other ambient environmental factors may change as well, and the sensitivity of other  
25 diazotrophic organisms to temperature is not known at present.

Mulholland (2007) reviews the literature on the fate of new nitrogen fixed by the diazotrophs. The key question she addresses is whether the carbon and nitrogen fixed by diazotrophs contribute to “new” or “regenerated” production? She summarizes the current knowledge of diazotrophic  $\text{N}_2$  and C fixation, nitrogen and carbon release and

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the trophic interactions with special emphasis on *Trichodesmium*.

### 3 Theme: losses of N from the ocean

With regard to losses of fixed nitrogen from the sea, in addition to the above-mentioned studies on anammox from the OMZs of the eastern tropical Pacific and Atlantic, a large amount of information has come from the Arabian Sea, which houses the other major oceanic OMZ. Naqvi et al. (2006) combine previously published data with new measurements to show the contrasts between the perennial open-ocean suboxic zone and the volumetrically smaller but more intense suboxic zone that develops seasonally over the western Indian shelf. One of the most interesting observations from the former region is the large mismatch between the excess  $N_2$  computed from the measured  $N_2/Ar$  ratio and the Redfield stoichiometry-based nitrate deficits (the latter being lower by a factor of 2). Anammox can account for only a part of this discrepancy and other factors (e.g. anaerobic degradation of non Redfieldian organic matter, presumably arising from  $N_2$  fixation) must also be important (Devol et al., 2006).

$N_2O$  cycling is also a subject of two other articles contributed to this issue by Walter and coworkers, the first from the North Atlantic and the second from the Baltic Sea. The North Atlantic data set presented by Walter et al. (2006a) is perhaps the most detailed and extensive collected from this region so far, enabling the preparation of basin-wide  $N_2O$  distribution maps at several isopycnal horizons. The trends of variability observed match expectations with the highest subsurface concentrations occurring in the eastern part of the tropical basin, and  $\Delta N_2O$  (difference between the observed and saturation values) values co-varying with the apparent oxygen utilization and nitrate. Observations in the Baltic (Walter et al., 2006b) were made about nine months after an inflow event from the North Sea had occurred in January 2003. This intrusion carried oxygen to the otherwise anoxic subsurface waters of the Baltic, and produced a patchwork of redox environments in the region, ranging from fully oxic to anoxic, and consequently large spatial variability in  $N_2O$  concentration. Some of the findings of

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this study are a bit unexpected and the  $\text{N}_2\text{O}$  concentrations generally lower than one would expect from the prevailing oxygen deficiency. That is,  $\text{N}_2\text{O}$  concentrations at the peripheries of the suboxic zone are much lower than those observed in the open ocean suboxic zones. However, a similar trend is also observed in the Black Sea (Westley et al., 2006), indicating different pathways of  $\text{N}_2\text{O}$  production in these enclosed basins.

Given the sensitivity of denitrification to minor changes in oxygen concentrations around the threshold value of  $\sim 1 \mu\text{M}$ , and also considering the large volume of water in the OMZs where the oxygen concentrations are marginally above this threshold, fluctuations in the oceanic denitrification rate on a short term basis are not only possible but very likely to occur. How quickly the feedback mechanisms within the ocean (e.g. enhanced  $\text{N}_2$  fixation) can respond to these changes is not known. If, on the other hand, the large imbalance between the losses and inputs estimated by Codispoti (200–300  $\text{Tg N yr}^{-1}$ ) persists, it should show up in high-resolution sedimentary  $\delta^{15}\text{N}$  records. Altabet (2007) uses a simple model to demonstrate that changing water column denitrification by  $\pm 30\%$  or  $\text{N}_2$  fixation by  $\pm 15\%$  produces  $> 1\%$  shifts in average oceanic  $\delta^{15}\text{N}$  on the time scale of nitrogen turnover in the ocean. Altabet also examines high resolution  $\delta^{15}\text{N}$  records from several sites considered to be sensitive to oceanic average  $\delta^{15}\text{N}$  and finds no detectable change over the last 3000 years, implying a balanced marine nitrogen budget through the latest Holocene. This would imply that either the losses of nitrogen from the ocean have increased in recent times or, as noted above, that we continue to underestimate the global rate of  $\text{N}_2$ -fixation in the ocean despite the upward revisions from 25  $\text{Tg N yr}^{-1}$  (Codispoti and Christensen, 1985) to 135  $\text{Tg N yr}^{-1}$  (Codispoti, 2007) over the last two decades.

#### 4 Theme: human impact and controls on the N cycle

Voss et al. (2006) use extensive data sets on chemical and dual stable isotopic composition of nitrate in several rivers draining into the Baltic Sea to identify the sources of nitrate in the river systems. Estimates of source attribution by emission models, Global

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Land Cover models and isotope mixing models were compared.

The Baltic, of course, is one of the regions where N cycle has been clearly and substantially altered by human activities. R. Elmgren's talk at the SPOT-ON meeting dealt with the complex nature of such impact arising from the riverine loading of N and P, loss of N due to denitrification in deep waters and associated mobilization of P that, in turn, favours blooms of the diazotrophs such as *Aphanizomenon* (Rolff et al., 2007; Moisander et al., 2007). In a system such as this, countering eutrophication would involve strong reductions of external and, if possible, internal loads of both P and N. Similar reductions of nutrient loading were also recommended by H. Paerl in his presentation that focused on effects of anthropogenic and climatic perturbations on nutrient-phytoplankton interactions and eutrophication in the Chesapeake Bay and the Neuse River Estuary, two highly eutrophied estuarine systems along the US coast (Paerl et al., 2007).

## 5 Theme: methodological advances

Presentations under this theme included development of new sensors and their application (by K. Johnson – Johnson et al., 2006), isotopomer measurements on N<sub>2</sub>O (by M. Westley and H. Yamagishi – Westley et al., 2006; Yamagishi et al., 2007) and several others involving application of molecular techniques.

Given the difficulty involved in culturing microbes that mediate various biogeochemical transformations including redox reactions of the N cycle, molecular tools have been found to be extremely useful to gain insights into the structure, functions and capabilities of these organisms (Zehr and Ward, 2002). There is a rapidly expanding database on phylogenetic diversity of natural denitrifying communities in both sediments and water column (e.g. Braker et al., 2000; Jayakumar et al., 2004). In this issue, Falk et al. (2007) compare denitrifying microbial communities across environmental gradients within the water column and coastal sediments of the Baltic Sea by employing one of the two nitrite reductase genes, *nirS*, as a molecular marker for denitrifiers. Phyloge-

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netic analysis of nirS genes from the Baltic Sea and of sequences from other areas indicate distinct denitrifier communities that seem to group mostly according to their habitats. They conclude that distinct marine nirS-type denitrifier communities developed after selection determined by their habitats, the ambient environmental conditions and isolation by large geographic distances between habitats.

P. Moisander reported on the development of a nifH oligonucleotide microarray that includes most of the known nifH sequences from various marine environments. The diazotrophic community structure in microbial mats from Guerrero Negro, Baja California, Mexico, has been studied using polymerase chain reaction amplification of the nifH gene and the nifH oligonucleotide microarray (Moisander et al., 2006). This allows comparison of relative numbers of the gene and transcripts of the dominant nitrogen-fixing taxa for determining the relative abundances and gene expression of each taxa.

Until very recently, dissolved organic nitrogen (DON) had been largely neglected as a potentially-important source of nitrogen for phytoplankton because of smaller variability relative to the inorganic fixed nitrogen pool. This view is now being revised as a result of development of newer techniques including the application of <sup>15</sup>N tracers. Bronk et al. (2007) present a synthesis of the rapidly accumulating evidence for the bioavailability of DON. While diatoms appear largely to utilize nitrate, other eukaryotic phytoplankton use reduced nitrogen forms and low molecular weight DON such as urea, amino acids and peptides. This review also provides an account of the enormous progress made in the molecular aspects of DON cycling, including the identification and characterization of functional genes encoding for key enzymes involved.

## 6 Theme: evolution and diversity of the N cycle

Although several talks were presented under this theme, including one by J. Brandes on the prebiotic and protobiotic origins of the global N cycle, and a number of others based on paleo-studies using stable isotope tracers (e.g. Brunelle et al., 2007), there is only one article included in this issue. The diazotrophic cyanobacteria are among the

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most ancient photoautotrophs. An example of their varying abundance in the geological past in response to environmental changes is provided by Ohkouchi et al. (2006). These authors determined the isotopic composition of the bulk sediment as well as geoporphyryns from the Livello Bonarelli black shale deposited during the Cretaceous Oceanic Anoxic Event 2 (OAE-2, ca. 94 Ma). Their results suggest that diazotrophic cyanobacteria were the major primary producers during the OAE-2, and probably also during similar events that intermittently occurred throughout the later half of the Earth's history.

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